FINAL REPORT

STATISTICAL THEORY OF ELECTRONIC ENERGIES

by

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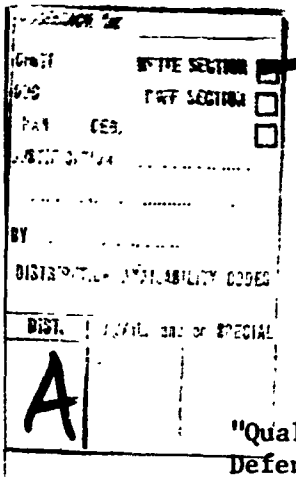

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13. ABSTRACT

An investigation of the effect of the imposition of various symmetries upon Thomas-Fermi Theory has been completed. The effect of projecting the density matrix into even and odd parts has been examined to first, second, and third order. A fundamental flow in Thomas-Fermi Theory, the fact that the density matrix is not Hermitian, has also been considered. This research leads to a relatively simple scheme for re-defining the exchange energy in Thomas-Fermi approximation. Anguler momentum projections and the effect of rising the temperature above zero degrees absolute has been studied.

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The concept of the work to be performed under this grant evolved considerably over the course of the grant period, so that many of the separate areas were seen to be part of a larger concept. This unifying principle was the density matrix.

The basic results found during the course of this work are three in number. First, in lowest Thomas-Fermi approximation, the eigenfunctions of the density matrix form an excellent approximation to the eigenfunctions of the true density matrix, but the eigenvalue spectrum is faulty. Thus, a much more useful theory may be had by the simple artifice of imposing upon the density matrix an eigenvalue spectrum appropriate to a self-consistent theory.

Second, as was originally proposed, it was found possible to construct a second order and higher order Thomas-Fermi theories that gave improved results. This involved investigation of the consequences of representing the statistical weight operator as an iterated product rather than as a series, as had been the practice. We were able to point out that the series representation would normally be expected to diverge, whereas the product representation has so for not misbehaved in any case, nor can any such possibility be envisaged now. In two nontrivial cases we were able to construct a hierarchy, or sequence, of Thomas-Fermi theories to an order n, and examine the behavior of the sequences in the limit of infinite n.

We have shown that in this limit, Thomas-Fermi theory gives the exact quantum mechanical result for the entire density matrix in these two cases. This permits us to state that the eigenvalues of the Thomas-Fermi density matrix should converge as $1/n^2$, where n is the order of approximation employed. We did not anticipate this accomplishment in the original proposal.

Of a good deal of practical utility, we believe, is our third result, which was likewise not anticipated in the original proposal. Upon examining the concept of exchange energy in Thomas-Fermi theory, we found that the assumption of a Hartree-Foch two particle reference state was sufficient to generate the usual Thomas-Fermi single particle exchange operator, which is proportional, as is well known, to the one-third power of the density, provided that the single particle density matrix used is assumed Hermitian and idempotent. Neither, in fact, is true. Upon re-defining the single particle density matrix as a Hermitian form, we were able to generate an expression for the single particle exchange operator as a functional of the density which gives much more accurate results than the previous expression when applied to Hartree-Foch densities of atoms. This should, if adopted generally by solid-state workers, improve greatly the accuracy of the method of Slater, currently very popular.

The one major area originally proposed for investigation that was not examined was the application of these techniques to finite temperature. Difficulties in finding competent personnel, particularly during the early stages of this work, and the greater immediacy in exploiting the results of our new-found understanding of the density matrix, are cited.

The attached list of papers were published or are in press as of this date. In addition, several manuscripts are in preparation.

George S. Handler
Principal Investigator

PAPERS PUBLISHED

1. Higher Order Thomas-Fermi Theories, George S. Handler, and Shigehiro Kobayashi in Queen's Papers on Pure and Applied Mathematics - No. 11, Queen's University, Kingston, Ontario (1968).

2. Statistical Two-Particle Density Matrix. Some Considerations Relating to the Choice of Basis of Representation, George S. Handler, J. Chem. Phys., 49, 3522-3526 (1968).

3. On the Energy of a Thomas-Fermi System, George S. Handler, J. Quant. Chem., Vol. 111S 703-706 (1970).

4. 2-Matrices from Thomas-Fermi Theory, George S. Handler, J. Quant. Chem., 4, 359-361 (1971).

5. Convergence of a Product Representation of the Exponential Hamiltonian Operator. An Example from Statistical Theory, George S. Handler and Pearl S. C. Wang, J. Chem. Phys., 4, 1546-1548 (1972).

PAPER IN PRESS

1. Eigenfunctions and Eigenvalues of the Thomas-Fermi Density Matrix. The Simple Harmonic Oscillator, George S. Handler and Virginia L. Benton, J. Chem. Phys.

PAPERS IN PREPARATION

1. Exchange Energy in Thomas-Fermi Theory, George S. Handler.

2. Chemical Binding in Thomas-Fermi Theory, George S. Handler.